

Use of polyanions for alkylation of hydrazine derivatives.

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Supporting material

All reagents were obtained from commercial sources and used without further purification. THF was freshly distilled from Na/benzophenone.

NMR spectroscopy was performed on a Bruker Avance II 200 200 MHz spectrometer using TMS as internal standard. Infrared spectra were measured on a Perkin-Elmer PC16 FTIR spectrometer, using KBr pellet technique for solid compounds and liquid film technique for oils. Melting points were determined on a Gallenkamp melting point apparatus. Compounds **2b,c** (**3a,b**) and **2d** are crystalline solids, others are oils.

Procedures:

Alkylation of trianion with 3 equiv of alkyl halide (**1a**); Typical procedure

An oven-dried flask was charged with BocNHNH₂ (2 mmol, 264 mg), then evacuated and backfilled with argon. Thereafter THF (14 mL) was added to dissolve the solid. Reaction mixture was cooled down to -78 °C and 1.6M n-BuLi (6.6 mmol, 4.13 mL) solution was added drop wise. Then reaction mixture was allowed to warm up to -40 °C for another 30 min and MeI (8 mmol, 0.5 mL) was added. Then reaction mixture was allowed to slowly warm up to room temperature. The reaction progress was monitored by TLC (Hexane:Et₂O 1:1). After 6 hours reaction was mainly complete, but it was allowed to stir overnight. Then volatiles were evaporated (ca. 150 mm Hg, 40 °C). To the resulting mixture 15 mL of DCM and 6 mL of brine were added. Organic fraction was separated and dried with MgSO₄. Then volatiles were removed (ca. 150 mm Hg, 40 °C) and residue was purified by column chromatography on silica (Hexane:Et₂O 2:1). 310 mg of colourless oil. Yield was 89%.

Alkylation of trianion with 2 equiv of alkyl halide (2a); Typical procedure

An oven-dried flask was charged with BocNHNH₂ (2 mmol, 264 mg), then evacuated and backfilled with argon. Thereafter THF (14 mL) was added to dissolve the solid. Reaction mixture was cooled down to -78 °C and 1.6M n-BuLi (6 mmol, 3.75 mL) solution was added drop wise. Then reaction mixture was stirred for 15 min and MeI (4 mmol, 0.25 mL) was added. The reaction progress was monitored by TLC (Hexane:Et₂O 1:1). Then reaction mixture was stirred for 1 h, then allowed to warm up to room temperature and stirred overnight. Then 0.1 mL H₂O was added and volatiles were evaporated. To the resulting mixture 10 mL of CHCl₃ and MgSO₄ was added. Then mixture was filtered and volatiles were removed. Residue was purified by column chromatography on silica (Hexane:Et₂O 1:1). 237 mg of colourless oil obtained. Yield was 74%.

Alkylation of dianion with 2 equiv of alkyl halide (3a); Typical procedure

An oven-dried flask was charged with BocNHNH₂ (2 mmol, 264 mg), then evacuated and backfilled with argon. Thereafter THF (10 mL) was added to dissolve the solid. Reaction mixture was cooled down to -90 °C and 1.6M n-BuLi (4 mmol, 2.5 mL) solution was added drop wise. Then reaction mixture was stirred for 15 min and AllBr (4 mmol, 0.35 mL) was added. Then reaction mixture was stirred for 1 h, then allowed to warm up to room temperature and stirred for another 1 h. The reaction progress was monitored by TLC (Hexane:Et₂O 1:1). Then 0.1 mL H₂O was added and volatiles were evaporated. To the resulting mixture 10 mL of CHCl₃ and MgSO₄ was added. Then mixture was filtered and volatiles were removed. The residue was purified by column chromatography on silica (Hexane:EtOAc 4:1). 284 mg of colourless crystals obtained. Yield was 67%.

Alkylation of dianion with 1 equiv of alkyl halide (4a); Typical procedure

An oven-dried flask was charged with BocNHNH₂ (2 mmol, 264 mg), then evacuated and backfilled with argon. Thereafter THF (5 mL) was added to dissolve the solid. Reaction mixture was cooled down to -90 °C and 1.6M n-BuLi (4 mmol, 2.5 mL) solution was added drop wise. Then reaction mixture was allowed to warm up to -50 °C for 20 min and AllBr (1 mmol, 0.09 mL) was added. Then reaction mixture was stirred for 1 h. The reaction progress was monitored by TLC (Hexane:EtOAc 4:1). Starting material and some amount of *tert*-butyl-2,2-diallylhydrazinecarboxylate was noticed. Then

another 0.5 equiv of AlIBr (1 mmol, 0.09 mL) was added. After 1 h 0.2 mL of MeOH was added followed by 0.2 mL H₂O. After that reaction mixture was allowed to warm up to room temperature. The reaction mixture was evaporated. To the resulting mixture 15 mL of DCM and 6 mL of brine were added. Organic fraction was separated and dried with MgSO₄. Then volatiles were removed and residue was purified by column chromatography on silica (Hexane:EtOAc 4:1). 175 mg of colourless oil obtained. Yield was 50%.

Analytical data:



¹H NMR (200 MHz, CDCl₃, TMS): δ = 2.91 (s, 6H), 2.61 (s, 3H), 1.48 (s, 9H).

¹³C NMR (100 MHz, CDCl₃, TMS): δ = 155.6, 79.9, 42.7, 33.0, 28.7.

FT IR ν (cm⁻¹): 2972, 2952, 2885, 1698, 1487, 1452, 1364, 1154, 768.



¹H NMR (200 MHz, CDCl₃, TMS): δ = 5.94-5.74 (m, 3H), 5.22-5.05 (m, 6H), 3.84 (broad s, 3H), 3.47 (broad s, 3H), 1.47 (s, 9H).

¹³C NMR (100 MHz, CDCl₃, TMS): δ = 155.1, 135.8, 135.2, 117.3, 116.4, 80.1, 58.1, 55.1, 28.7.

FT IR ν (cm⁻¹): 3080, 2977, 2930, 2859, 1693, 1374, 1246, 1179, 1130, 994, 927, 763.

HRMS (ESI): m/z calcd for C₁₄H₂₄N₂O₂ [MH]⁺: 253.19105; found: 253.19110.



¹H NMR (200 MHz, CDCl₃, TMS): δ = 5.65 (broad s, 1H), 2.58 (s, 6H), 1.46 (s, 9H).

¹³C NMR (100 MHz, CDCl₃, TMS): δ = 154.7, 80.0, 47.6, 28.4.

FT IR ν (cm⁻¹): 3244, 2982, 2864, 2787, 1708, 1518, 1451, 1251, 1159, 1107, 846.



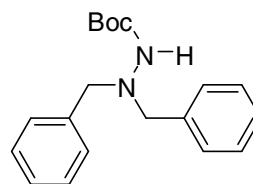
¹H NMR (200 MHz, CDCl₃, TMS): δ = 6.01-5.81 (m, 2H), 5.53 (broad s, 1H), 5.26-5.15 (m, 6H), 3.42/3.39 (s, 4H), 1.43 (s, 9H),

¹³C NMR (100 MHz, CDCl₃, TMS): δ = 155.3, 134.2, 118.4, 79.7, 59.8, 28.4.

FT IR ν (cm^{-1}): 3249, 3080, 2982, 2920, 2859, 1703, 1503, 1359, 1241, 1164, 995, 907, 845, 742, 614.

HRMS (ESI): m/z calcd for $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_2$ $[\text{MH}]^+$: 213.15975; found: 213.15965

mp 38-40 °C



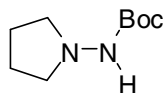
tert-butyl 2,2-dibenzylhydrazinecarboxylate (2c)

^1H NMR (200 MHz, CDCl_3 , TMS): δ = 7.40-7.24 (m, 10H), 5.68 (broad s, 1H) 4.05 (broad s, 2H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3 , TMS): δ = 155.2, 137.7, 129.3, 128.3, 127.3, 79.8, 60.4, 28.4.

FT IR ν (cm^{-1}): 3305, 3090, 3064, 3034, 2977, 2936, 2869, 2828, 1693, 1508, 1456, 1364, 1266, 1236, 1153, 742, 691.

mp 115-118 °C



tert-butyl pyrrolidin-1-ylcarbamate (2d)

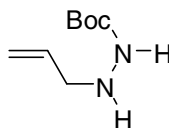
^1H NMR (200 MHz, CDCl_3 , 21 °C, TMS): δ = 5.62 (s broad, 1H), 2.87 (m, 4H), 1.82 (m, 4H), 1.46 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3 , 21 °C, TMS): δ = 155.0, 79.9, 55.1, 28.5, 22.4.

FT IR ν (cm^{-1}): 3229, 2977, 2925, 2843, 1688, 1544, 1282, 1359, 1164, 860, 624.

HRMS (ESI): m/z calcd for $\text{C}_9\text{H}_{18}\text{N}_2\text{O}_2$ $[\text{MH}]^+$: 187.14410; found: 187.14421

mp 110-114 °C



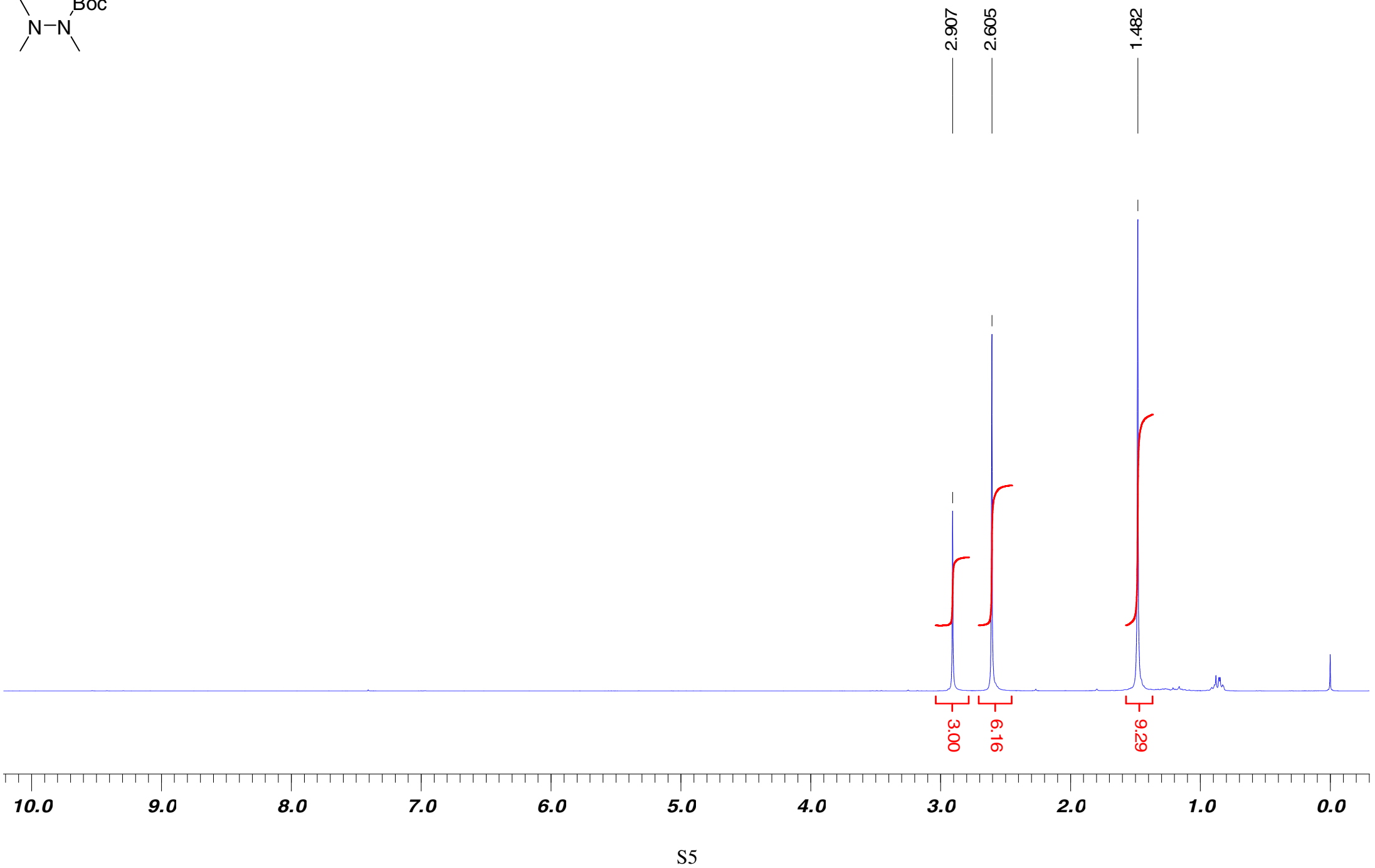
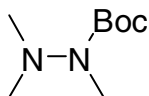
tert-butyl 2-allylhydrazinecarboxylate (4a)

^1H NMR (200 MHz, CDCl_3 , 21 °C, TMS): δ = 6.71/6.47 (broad s, 1H), 5.98-5.76 (m, 2H), 5.26-5.12 (m, 2H), 3.97 (s, 1H), 3.48/3.45 (s, 2H), 1.46 (s, 9H),

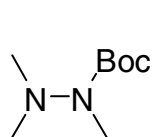
^{13}C NMR (100 MHz, CDCl_3 , 21 °C, TMS): δ = 156.8, 134.5, 117.9, 80.3, 54.6, 28.4.

FT IR ν (cm^{-1}): 3311, 3075, 2972, 2930, 2864, 1703, 1456, 1380, 1282, 1251, 1158, 927.

tert-butyl 1,2,2-trimethylhydrazinecarboxylate (1a)



tert-butyl 1,2,2-trimethylhydrazinecarboxylate (1a)



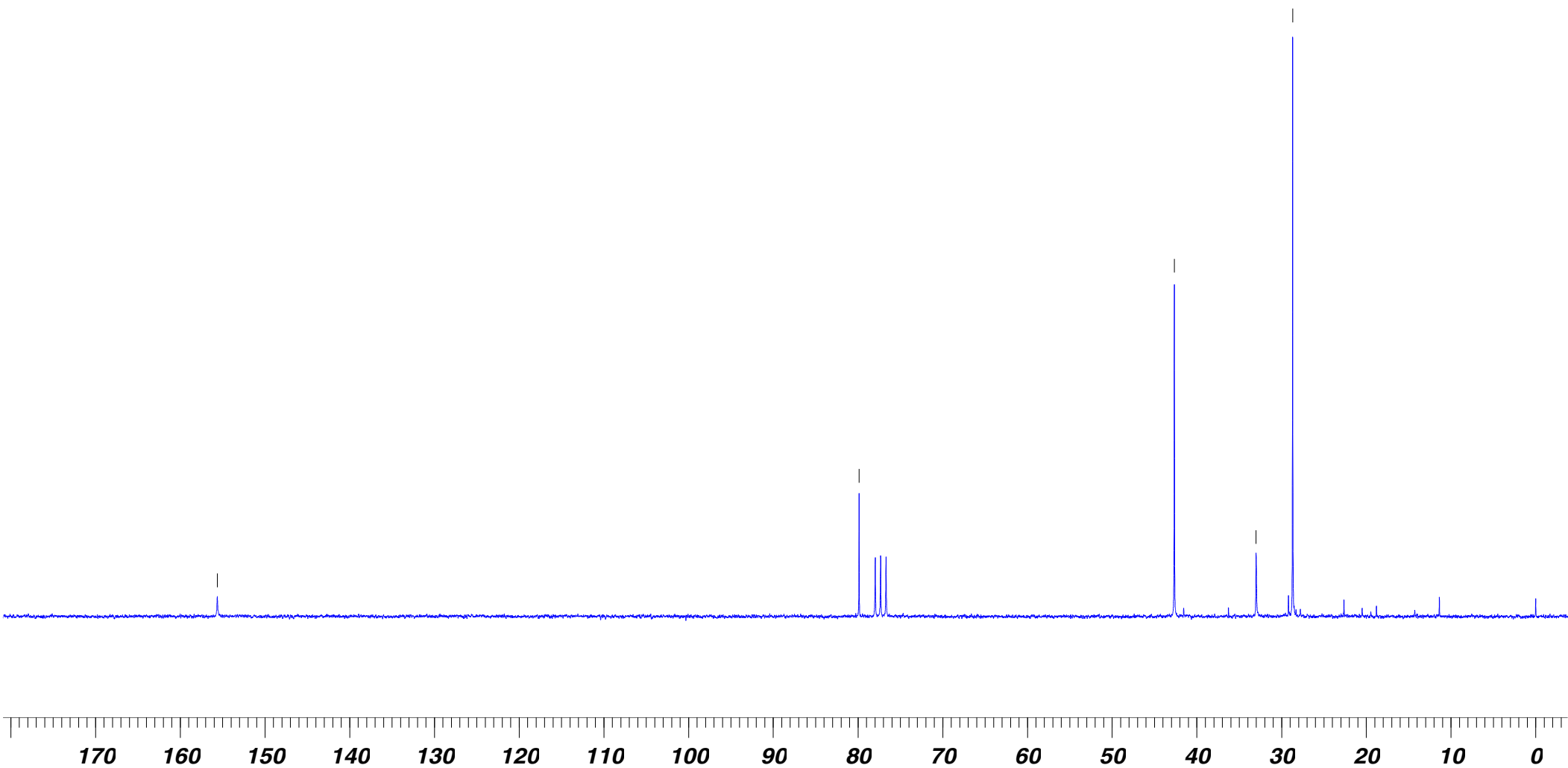
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79.863

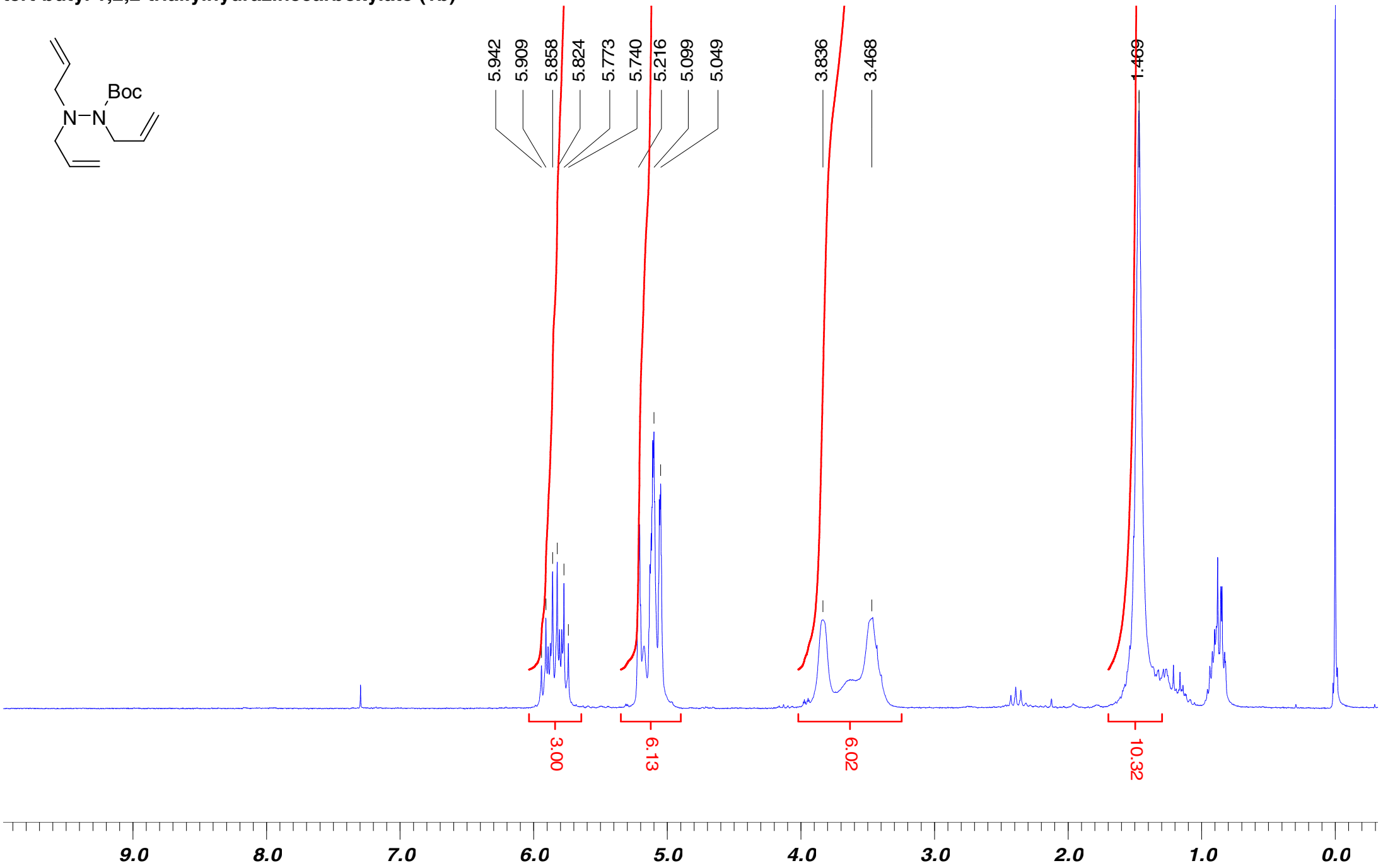
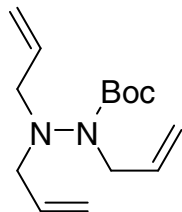
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33.005

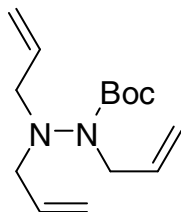
28.687



tert-butyl 1,2,2-triallylhydrazinecarboxylate (1b)



tert-butyl 1,2,2-triallylhydrazinecarboxylate (1b)



155.076

135.826

135.242

117.313

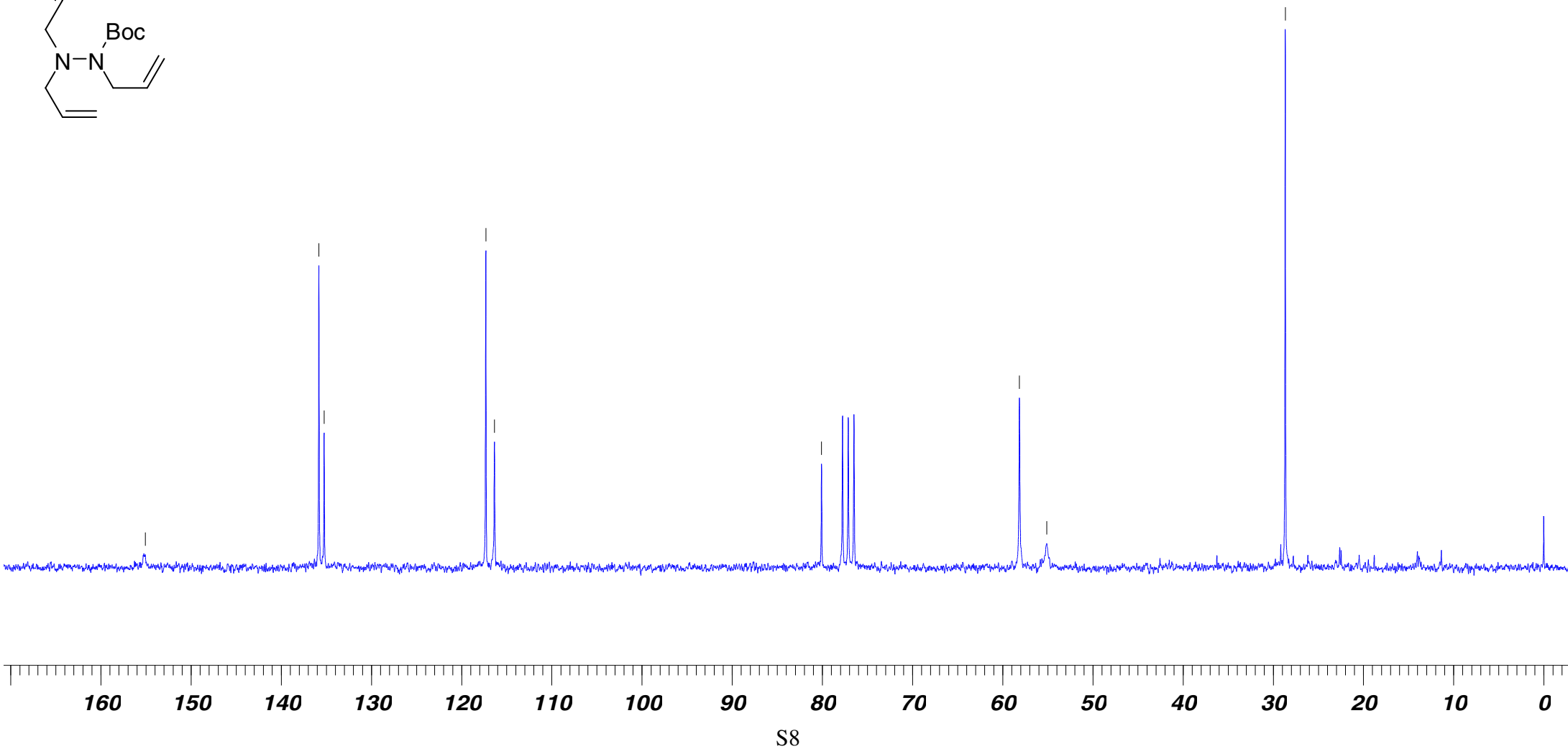
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80.089

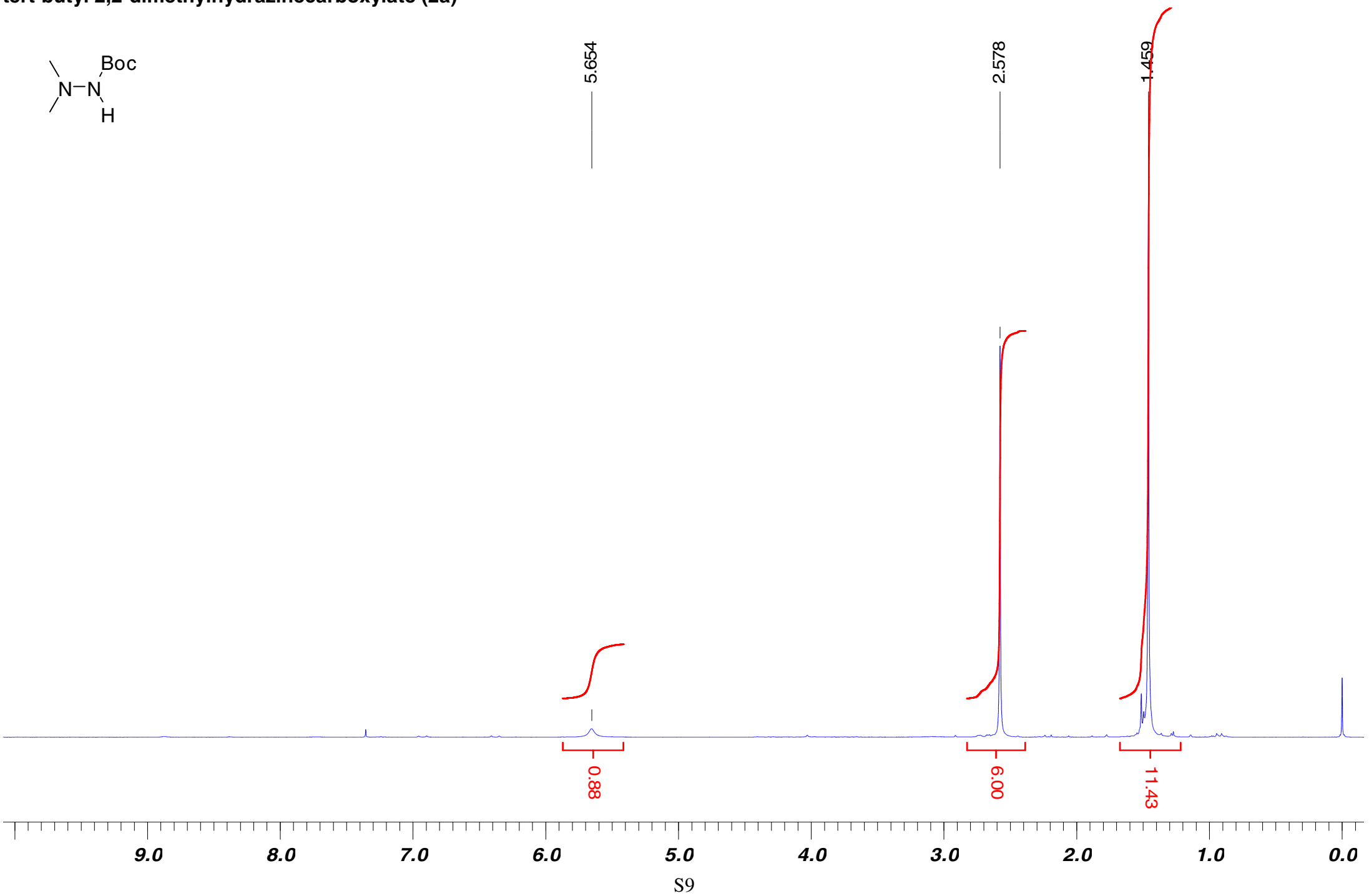
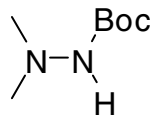
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55.114

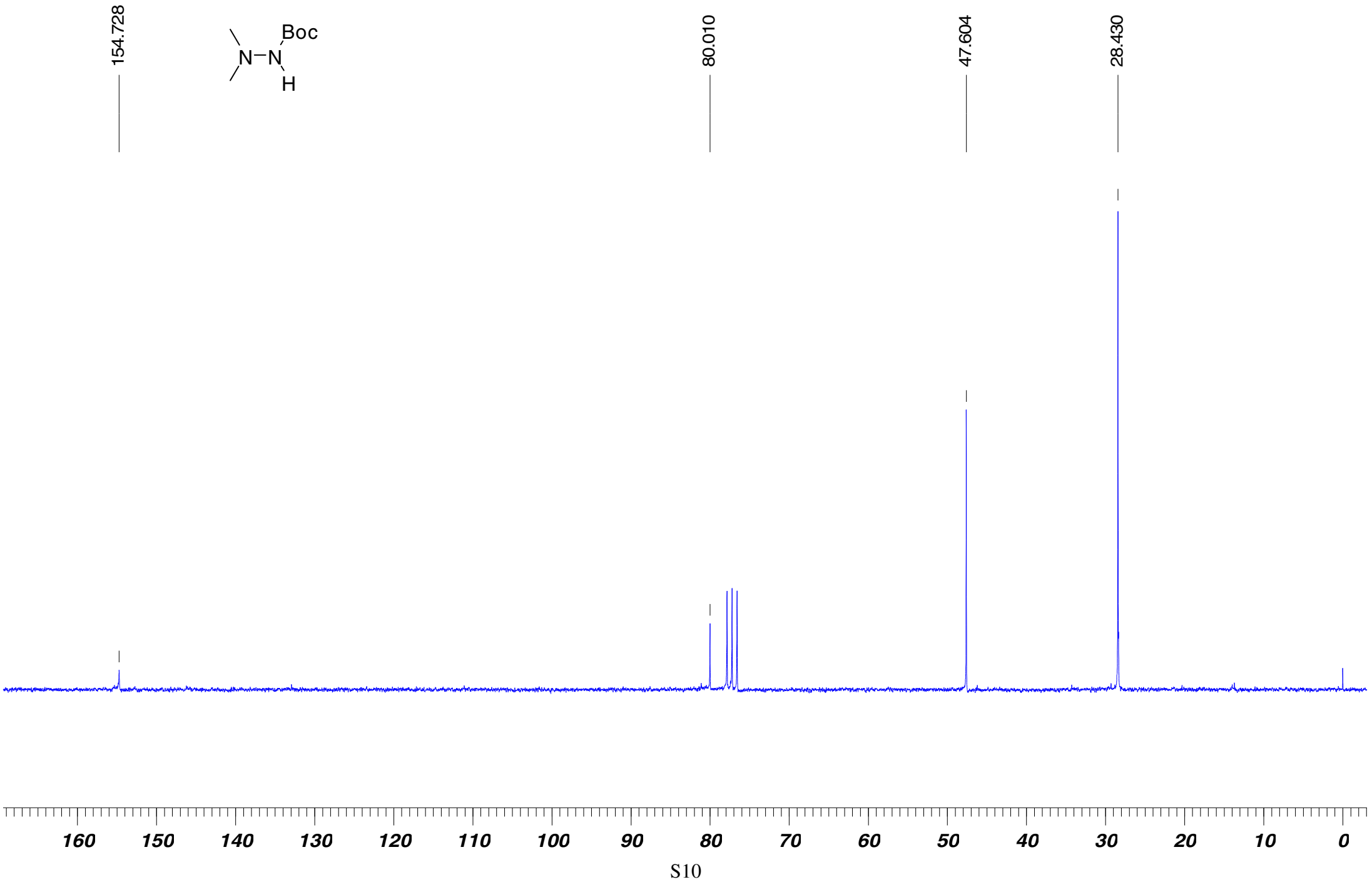
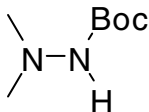
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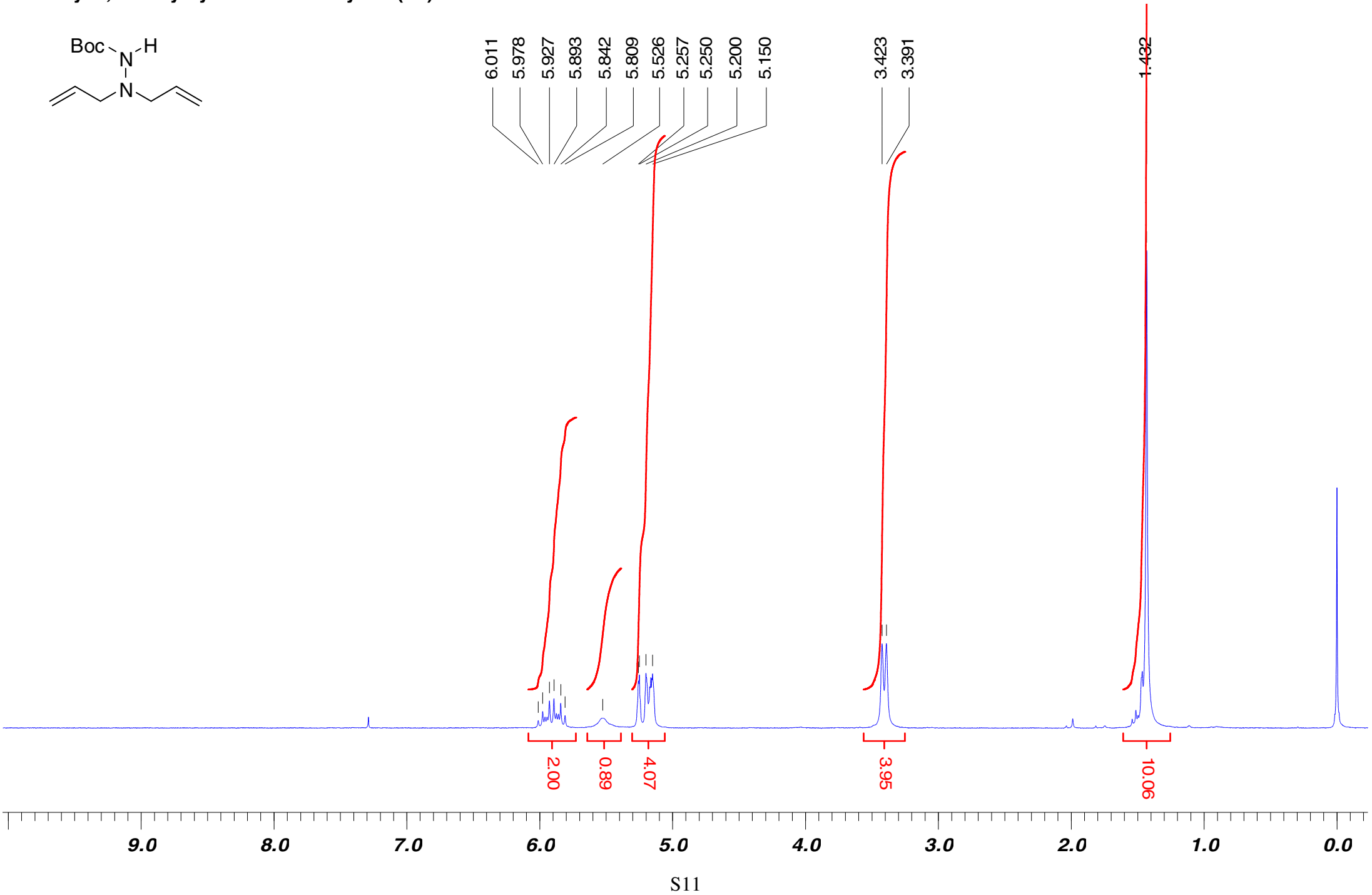
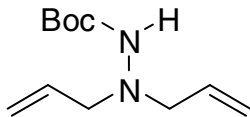
tert-butyl 2,2-dimethylhydrazinecarboxylate (2a)



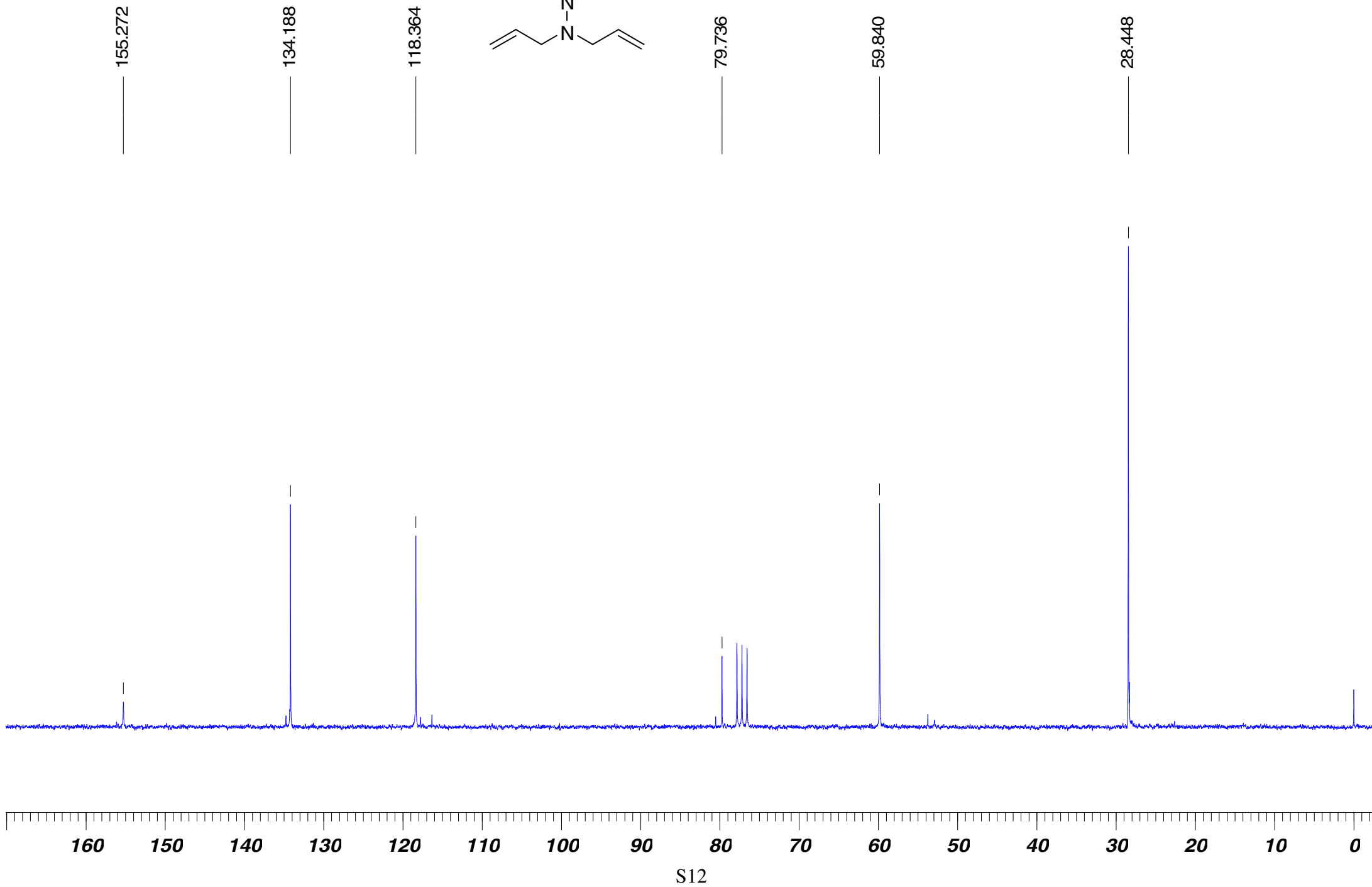
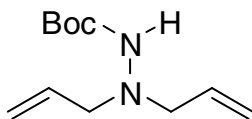
tert-butyl 2,2-dimethylhydrazinecarboxylate (2a)



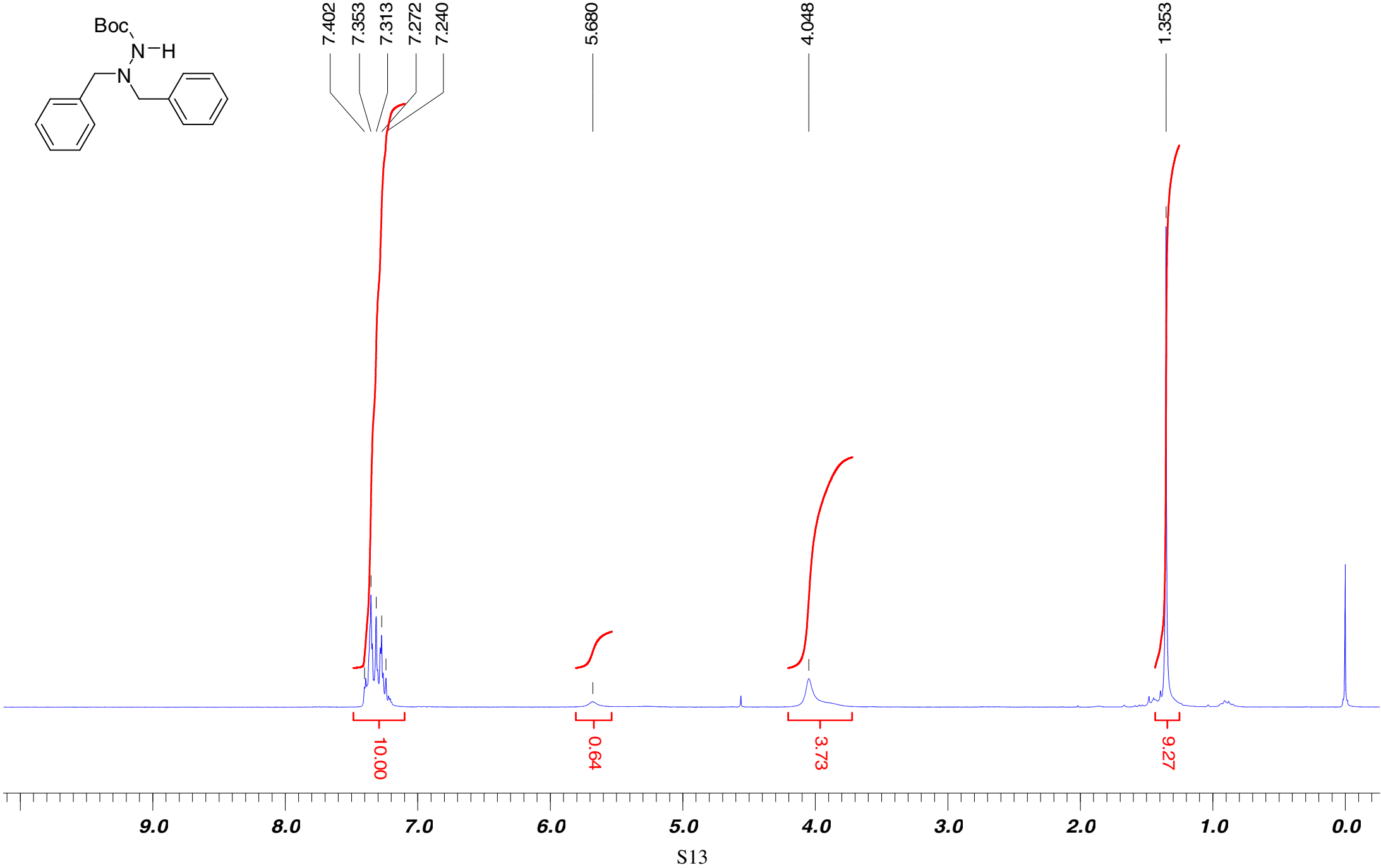
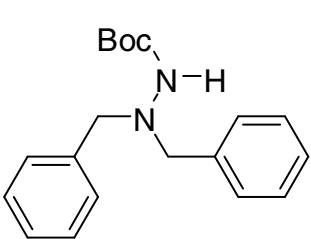
tert-butyl 2,2-diallylhydrazinecarboxylate (2b)



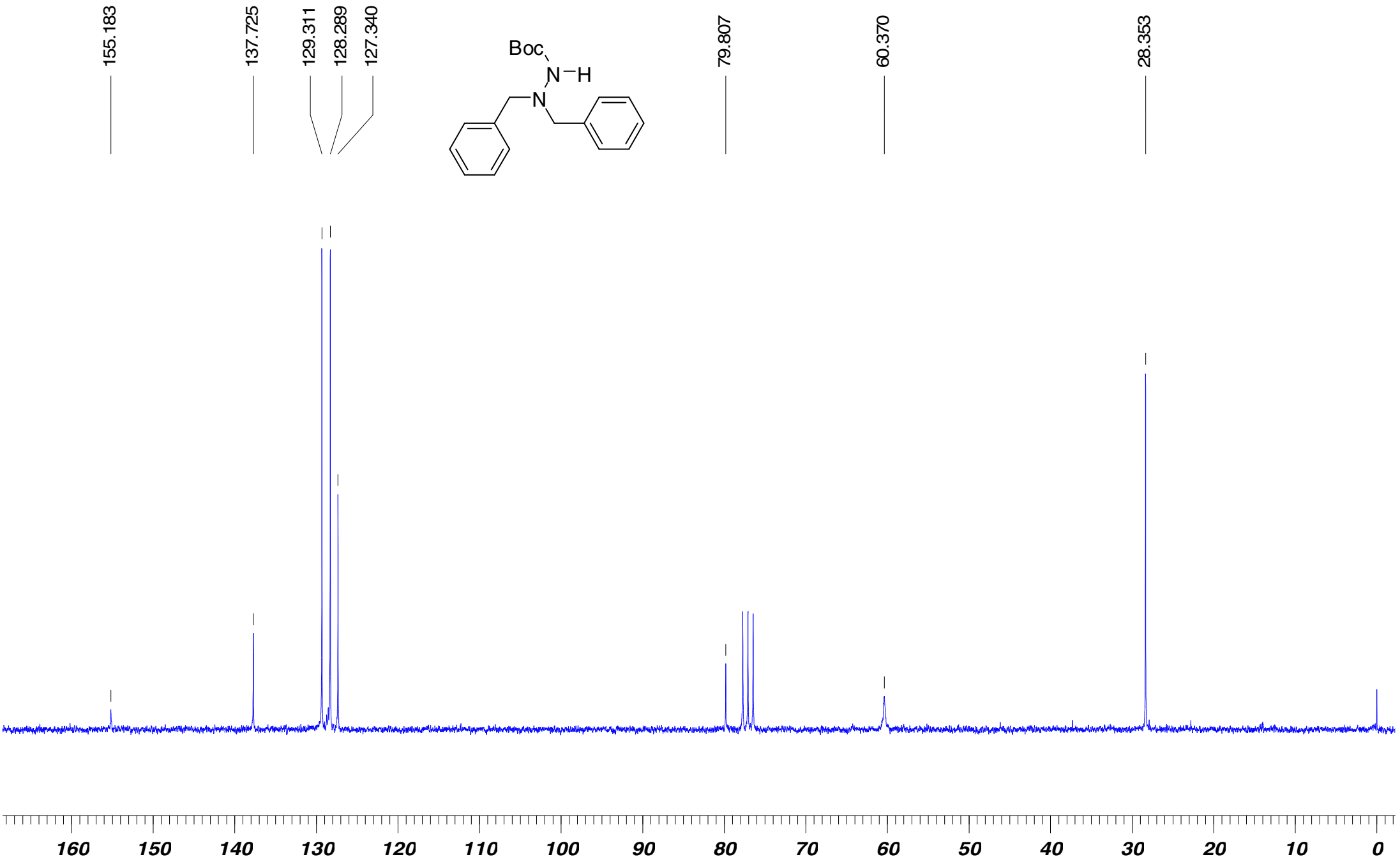
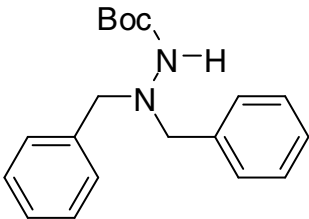
tert-butyl 2,2-diallylhydrazinecarboxylate (2b)



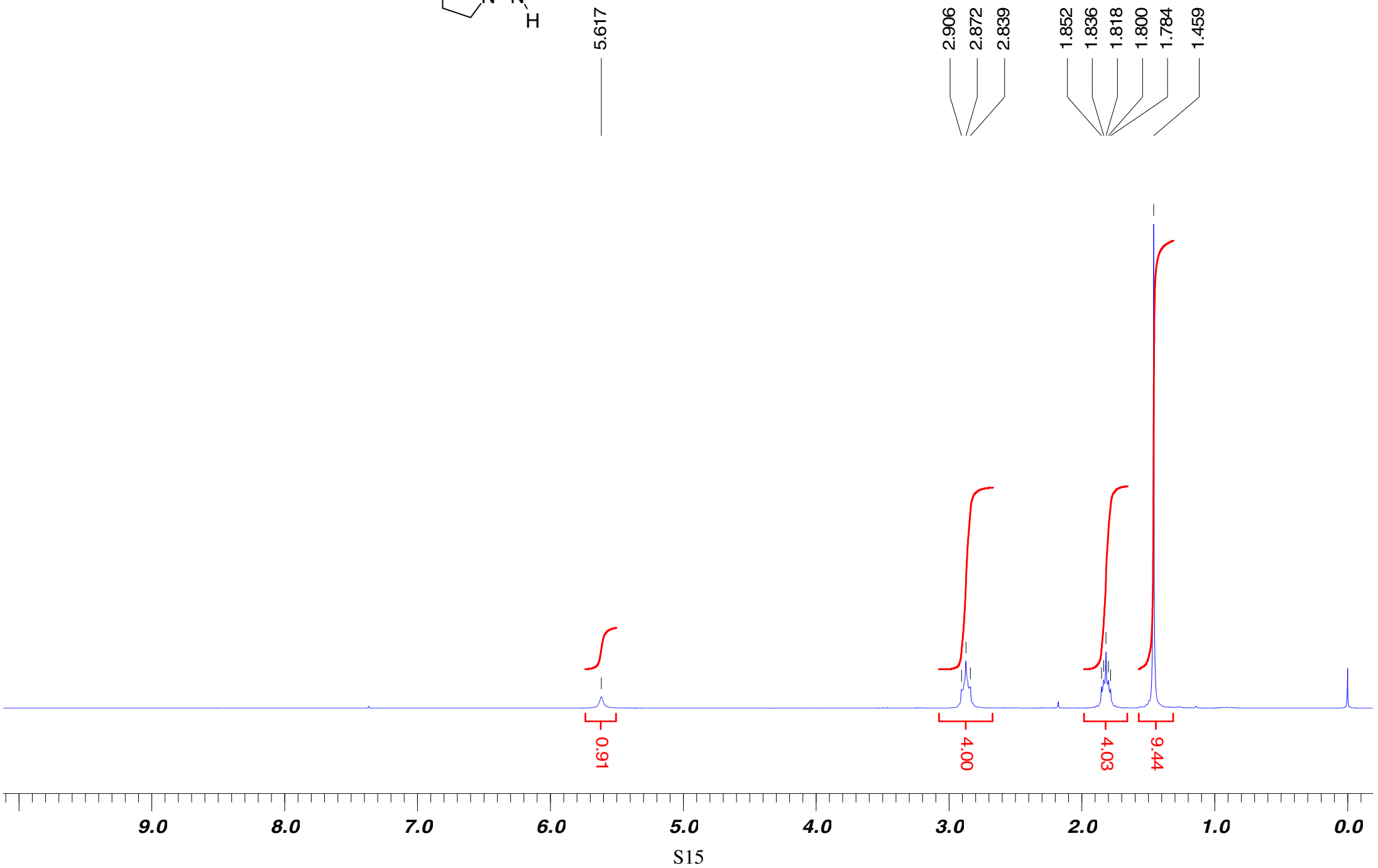
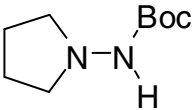
tert-butyl 2,2-dibenzylhydrazinecarboxylate (2c)



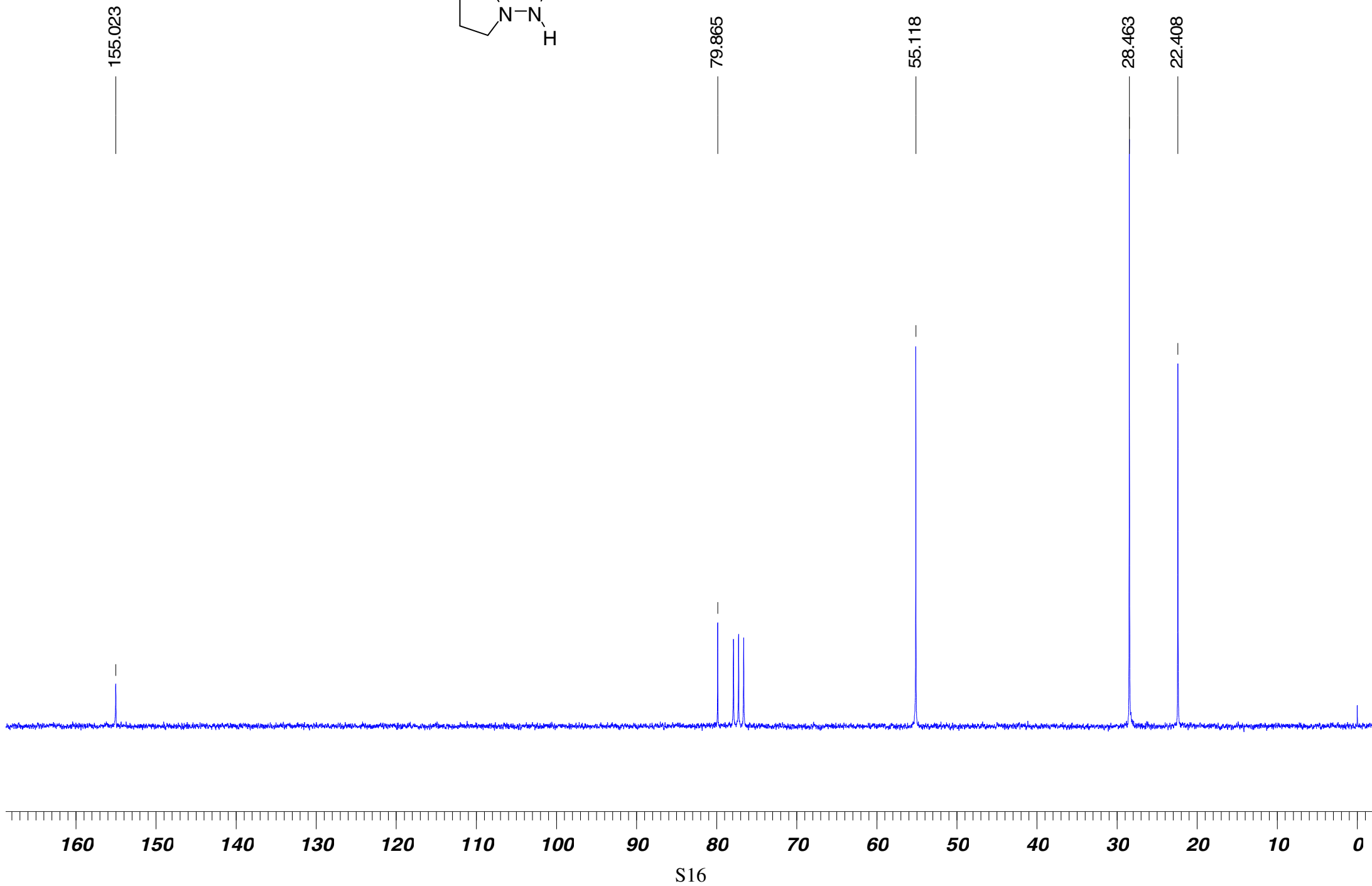
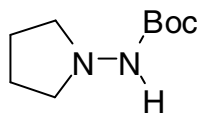
tert-butyl 2,2-dibenzylhydrazinecarboxylate (2c)



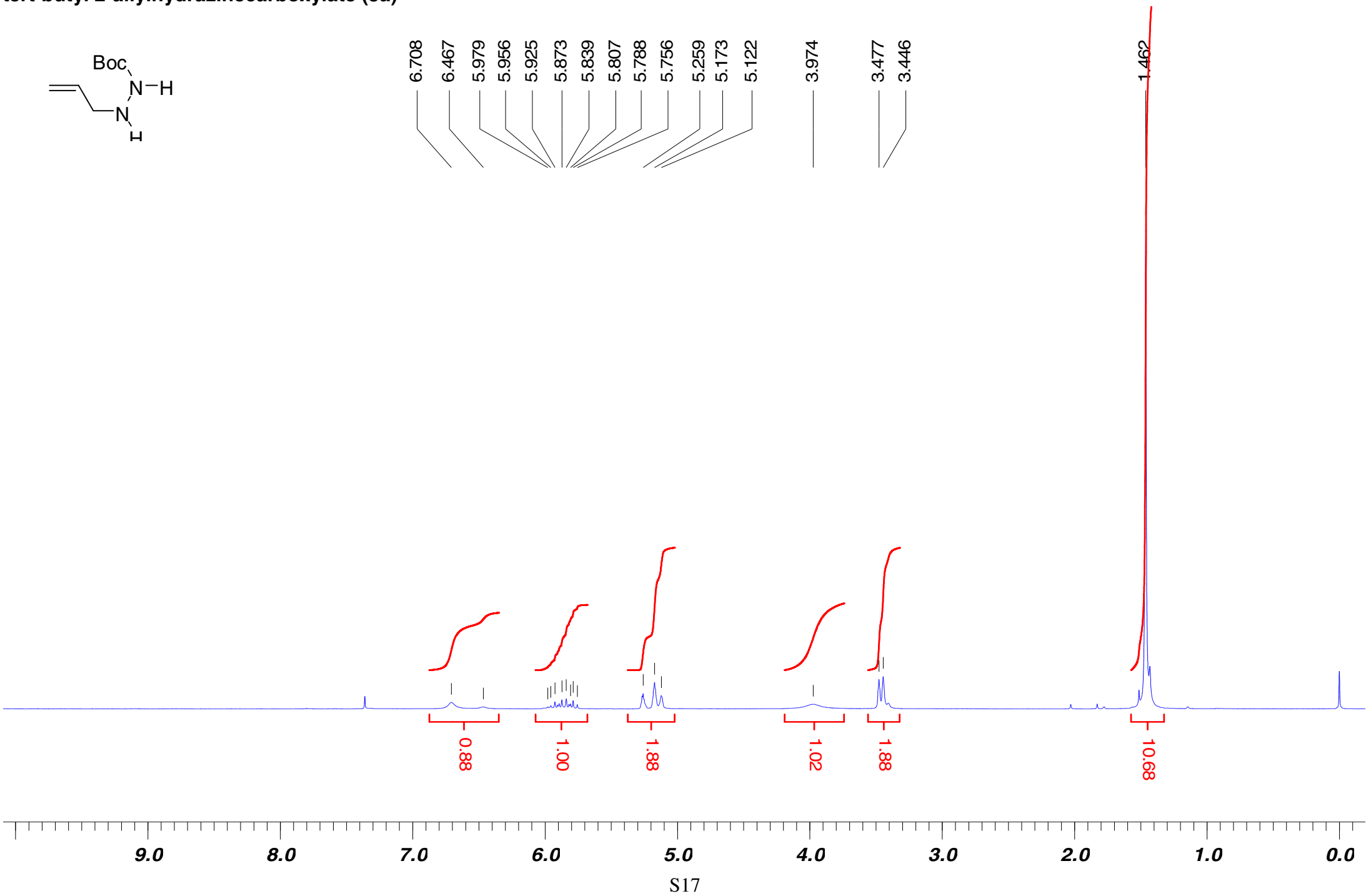
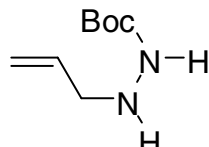
tert-butyl pyrrolidin-1-ylcarbamate (2d)



tert-butyl pyrrolidin-1-ylcarbamate (2d)



tert-butyl 2-allylhydrazinecarboxylate (3a)



tert-butyl 2-allylhydrazinecarboxylate (3a)

